the calculated values and residuals for all samples analyzed. The equation and appropriate coefficients have been used to generate the more convenient Tables VI–XVI. These tables represent commercial products in terms of D.E. (where appropriate) and ash levels, and are much more detailed in their expression of the dry substance dependence of refractive index.

Table XV for high fructose corn syrup was calculated in a similar manner even though the product is ordinarily not characterized by D.E. Sample 10 contained 93.1% (dry basis) dextrose plus fructose, and the observed D.E. was 94.1. Table XV represents a product containing 94.0% (dry basis) dextrose plus fructose, and has a calculated D.E. value of 94.6.

Correction factors for small variations in temperature, ash, and D.E. are given in Tables XVII and XVIII. The refractive index and dry substance values in Tables VI through XVI, higher than the experimental data originally obtained, were extrapolated within reasonable limits using eq 1 and the coefficients listed in Table V. Interpolation for intermediate values of dry substance should be easy and obvious.

Conclusions

Careful experimental work and extensive data analysis have been combined to produce accurate and useful tables, detailing the relationship between refractive index and dry substance content for a wide range of commercial corn syrups and maltodextrin. With these tables, measurements of refractive index may be used to obtain the dry substance content of corn syrups and maltodextrin solutions with speed, precision, and accuracy comparable to that of the vacuum oven–filter aid method.

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Thermodynamics of the System H₂O–NaH₂PO₄–H₃PO₄

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The excess free energies of mixing for the system H₂O–NaH₂PO₄–H₃PO₄ have been determined from vapor pressure measurements at 273.15 and 298.15 K. They are the same at the two temperatures, and, in common with other phosphate mixtures studied to date, are negative.

Mixtures of orthophosphoric acid with simple water-soluble salts are important models for phosphate fertilizers. Furthermore, such systems are of considerable theoretical interest because of the atypical behavior they exhibit which results from hydrolysis of the orthophosphate anion. The existence in phosphate solutions of the dimer $(H_2PO_4)_2{}^{2-}$ has been demonstrated by free energy measurements made in this laboratory (9), and, in view of the recent interest shown in phosphates in mixed-salt solutions (5, 8), it seems appropriate to have data on a mixture of a simple phosphate salt with phosphoric acid. The solubility diagram for the aqueous system NaH₂PO₄–H₃PO₄ has been reported on (4) but, although water activities also are plotted in the diagram, they are unfortunately not given with sufficient precision to permit the calculation of free energies. For this reason, I have redetermined the water activities in this system.

Experimental Section

The method used was that in the previous papers in this series (1, 2, 6, 7) (I neglected to refer to ref 2 in ref 7; in the region of overlap our results for $\phi(H_3PO_4)$ agree to within 0.01.) and in addition to the 298 K measurements, a further few measurements were made at 273 K. The isopiestic concentrations are given in Table I, with the phosphoric acid treated as a 1–1 electrolyte. A power series in I, the ionic strength of each mixture, was fitted to the data, using the expression:

$$(2y_A + k_B y_B)\phi - 2y_A \phi_A{}^0 - k_B y_B \phi_B{}^0 = y_A y_B(b_{01} I + b_{02} I^2) \tag{1}$$

where k_B, a constant characteristic of the electrolyte, is 2. As explained in the discussion, the data were recalculated after treating the H₃PO₄ as, next, a 1–2 electrolyte ($k_B = 1$) and, finally, a 1–3 electrolyte ($k_B = \frac{2}{3}$). This, of course, necessitated a recalculation of the y and ϕ values in each case. The b coefficients in eq 1 are related to the excess Gibbs energy of mixing in the system $\Delta_m G^E$ through Friedman's g_0 function (2)

$$b_{01} + \frac{1}{2}b_{02} = g_0 = \Delta_m G^E/(RTI^2 y_A y_B) \tag{2}$$

The values for the mixtures are plotted in Figure 1 for the three

Table I. Isopiestic Concentrations for $H_2O-NaH_2PO_4$ (A)-H_3PO_4 (B) at 298 K

m_{NaCl}	m	y_B	ϕ	g_0
		At 298 K		
0.1706	0.1776	0	0.8895	
	0.1955	0.2020	0.8080	−0.560
	0.2020	0.2736	0.7819	−0.538
	0.2195	0.4512	0.7195	−0.546
0.4401	0.4889	0	0.8284	
	0.5649	0.3076	0.7168	−0.273
	0.6042	0.4505	0.6702	−0.272
	0.6964	0.8104	0.5815	−0.277
0.6020	0.6903	0	0.8050	
	0.7598	0.2020	0.7313	−0.215
	0.7853	0.2736	0.7076	−0.216
	0.8468	0.4512	0.6562	−0.207
0.6484	0.7498	0	0.7994	
	0.8669	0.3076	0.6914	−0.209
	0.9215	0.4504	0.6505	−0.209
	1.0284	0.8104	0.5828	−0.187
0.6546	0.7547	0	0.8018	
	1.0332	0.7692	0.5856	−0.200
	1.0274	0.7756	0.5890	−0.160
	1.0555	0.8760	0.5733	−0.198
1.4772	1.9743	0	0.7146	
	2.1060	0.1790	0.6699	−0.149
	2.1315	0.2094	0.6619	−0.151
	2.3322	1.0	0.6049	
1.9470	3.099	0.7692	0.6158	−0.136
	3.077	0.7756	0.6202	−0.128
2.5862	3.818	0	0.6898	
	4.022	0.1790	0.6549	−0.134
	4.057	0.2094	0.6493	−0.136
	3.917	1.0	0.6724	
4.059	6.334	0	0.7179	
	6.784	0.3076	0.6702	−0.129
	6.764	0.4505	0.6722	−0.126
	6.236	0.8104	0.7292	−0.115
6.144	9.595	0.7692	0.8209	−0.115
	9.466	0.7756	0.8320	−0.108
	9.224	0.8760	0.8539	−0.112
		At 273 K		
1.0419	1.3240	0	0.7204	
	1.6086	0.7692	0.5930	−0.163
	1.5985	0.7756	0.5967	−0.150
	1.6166	0.8760	0.5901	−0.170
1.4117	1.9002	0	0.6877	
	2.0892	0.3076	0.6255	−0.147
	2.1375	0.4505	0.6114	−0.142
	2.1489	0.8104	0.6081	−0.131
3.647	5.475	0	0.7006	
	5.385	0.7692	0.7123	−0.127
	5.341	0.7756	0.7182	−0.121
	5.222	0.8760	0.7345	−0.125

different values of k_B. The g_0 values were calculated by ignoring the relatively low precision data for $I < 1.5$ and, when this was done, the average difference between the fitted straight lines and the experimental data was ±0.003 in ϕ. This compares well with the average difference between my single-salt data and the smoothed literature (1) data, of ±0.002 for NaH_2PO_4, thus indicating that the imprecision and the inaccuracy are of comparable magnitude. The few mixed salt measurements at 273 K gave g_0 values which were indistinguishable from the 298 K values.

Results and Conclusions

The behavior of phosphoric acid can best be explained if it is treated as a 1–1 electrolyte (5), but it can also formally be treated as a 1–2 or a 1–3 electrolyte. If the experimental mixing data reported in Table I are recalculated so as to include these latter two possibilities, two new sets of g_0 values emerge; all three of the possible sets of g_0 values are plotted in Figure 1. The increased imprecision represented by the larger symbols at the lower concentrations is indicative of the difficulty of obtaining precise low concentration isopiestic results.

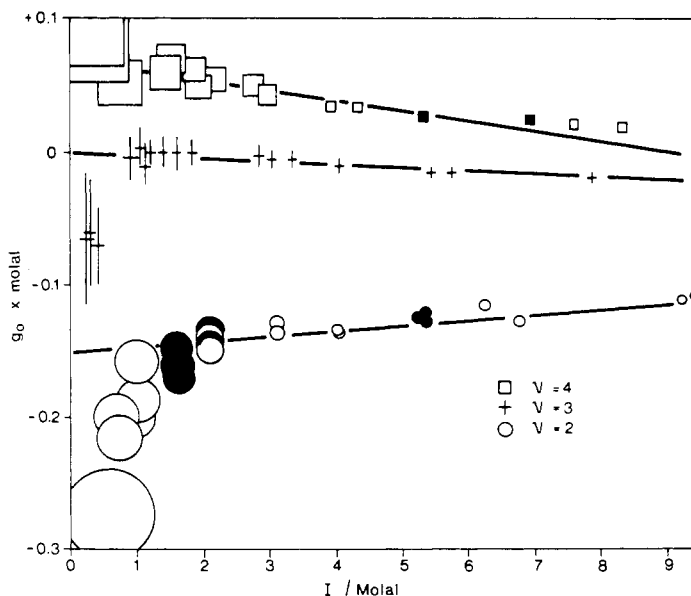Treating the acid as a 1–2 electrolyte produces, at moderate

Figure 1. Deviation function for the system $H_2O-NaH_2PO_4-H_3PO_4$ at 298 K, with H_3PO_4 treated as a 1–3 electrolyte (squares), as a 1–2 electrolyte (crosses), and as a 1–1 electrolyte (circles). Solid symbols refer to a temperature of 273 K.

concentrations, the smallest g_0, and therefore the smallest free energies of mixing, and such a treatment thus involves the smallest change in numbers of ion pairs during mixing.

If, however, the acid is treated as a 1–1 electrolyte, as previous work suggests it should be, the behavior of this system becomes consistent with the two previously studied common-anion phosphate mixtures, NaH_2PO_4 + KH_2PO_4 (1), and Na_2HPO_4 + $(NH_4)_2HPO_4$ (6), both of which exhibited negative excess Gibbs energies of mixing. The value for the mixing of NaH_2PO_4 + H_3PO_4, however, is very much more negative (−93J kg^{-1} at I = 1) than for either NaH_2PO_4 + KH_2PO_4 (−14J kg^{-1} at I = 1) or Na_2HPO_4 + $(NH_4)_2HPO_4$ (−4 J kg^{-1} at I = 1). Such large values could be explained by the existence of unlike cation pairs (such as Na^+-H^+), but this is unlikely. A more plausible explanation is that the mixing results in the generation of bulk solvent water, such as would be caused by dehydration of some phosphate polymer. This has the same effect as forming unlike cation pairs, or destroying like cation pairs, during the mixing process.

Glossary

y_A, y_B	ionic strength fractions of NaH_2PO_4 and H_3PO_4, respectively
ϕ	molal osmotic coefficient of mixed-salt solution
ϕ_A^0, ϕ_B^0	osmotic coefficient of single-salt solutions of NaH_2PO_4 and H_3PO_4
I	molal ionic strength of mixing, keeping in mind that each solution containing H_3PO_4 had three values, depending on whether it was treated as a 1–1, a 1–2, or a 1–3 electrolyte

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